

## Nanoscale High Energetic Materials: A Polymeric Nitrogen Chain $N_8$ Confined inside a Carbon Nanotube

Hakima Abou-Rachid,<sup>1,\*</sup> Anguang Hu,<sup>2</sup> Vladimir Timoshevskii,<sup>2</sup> Yanfeng Song,<sup>3</sup> and Louis-Simon Lussier<sup>1</sup>

<sup>1</sup>*Defence R&D-Canada, Valcartier 2459 Blv. Pie-XI North, Quebec, QC, Canada, G3J 1X5*

<sup>2</sup>*Quantum modeling Inc., 1255 rue University, Suite 608, Montreal, QC, Canada, H3B 3V9*

<sup>3</sup>*Q-Science Inc., 8331 Rue Ouimet, Brossard, QC, Canada, J4Y 3B4*

(Received 20 August 2007; published 13 May 2008)

We present a theoretical study of a new hybrid material, nanostructured polymeric nitrogen, where a polymeric nitrogen chain is encapsulated in a carbon nanotube. The electronic and structural properties of the new system are studied by means of *ab initio* electronic structure and molecular dynamics calculations. Finite temperature simulations demonstrate the stability of this nitrogen phase at ambient pressure and room temperature using carbon nanotube confinement. This nanostructured confinement may open a new path towards stabilizing polynitrogen or polymeric nitrogen at ambient conditions.

DOI: [10.1103/PhysRevLett.100.196401](https://doi.org/10.1103/PhysRevLett.100.196401)

PACS numbers: 71.10.-w, 73.22.-f

*Introduction.*—Current interest in polymeric nitrogen or polynitrogen as an explosive or propellant is largely driven by expectations that these molecules can function with an increased energy density [1], while decomposing into pure inert gas  $N_2$  molecules, which are environmentally safe, due to a uniquely large amount of the energy difference between single  $N-N$  or double  $N=N$  and triple  $N\equiv N$  bonds. For instance, the energy density of single-bonded polymeric nitrogen has been estimated to be at least 3 times higher than that of the most powerful energetic materials known today [2]. Several forms of polymeric nitrogen have been predicted theoretically [3], but only one of them, the so-called cubic *gauche* (CG) form, has been reported in 2004 to experimentally observed but at very high pressure and temperature conditions [1].

Recently, several new phases of polymeric nitrogen have been predicted theoretically [4,5]. These phases feature linear chainlike arrangements of nitrogen atoms as building blocks of three-dimensional crystals. Some of them were shown to be thermodynamically competitive with the CG phase, but none of them was shown to be stable at ambient conditions. Furthermore, all most theoretically predicted metastable polymeric nitrogen phases are subject to mechanical confinement conditions, high pressure. Theoretically to determine whether polymeric nitrogen could be experimentally observed at ambient condition, the effects of defects and surfaces on the metastability should be considered [6]. On this point, *ab initio* molecular dynamic simulations would be amenable combined with temperature effects within a supercell polymeric nitrogen system.

The field of nanostructured energetic materials is another highly active area of exploration [7–9], with emphasis on developing a fundamental understanding of size dependent material properties, as well as the novel interaction and functionality of the material at the molecular

level. Paramount to these developments is the requirement of high energy storage and its controlled release. Experimentally, work has progressed in the area of nanoscale energetic material preparation and characterization, with the focus primarily on controlling the uniformity of structure [7,8], functionalization [8], and assessing the performance of the material [7]. On the computational side, the challenge has been to provide simulation capabilities that can effectively assess the energetics, structure, and stability of candidate nanostructured energetic materials, while incorporating the quantum-confinement inherent in these materials. During the last few years it has become clear that first-principles electronic structure methods are capable of high accuracy prediction for molecular and solid properties in energetic materials over a wide range of conditions.

In this Letter we present an *ab initio* study of a stable form of polymeric nitrogen at ambient conditions of the temperature and pressure—a *nanostructured polymeric nitrogen*. It is a hybrid material where a polymeric nitrogen chain resides inside a carbon nanotube. We demonstrate that carbon nanotubes are ideal candidates to host polymeric nitrogen chains, and the hybridization between the nanotube and the N-chain conduction bands leads to the stability of the polymeric nitrogen at ambient conditions.

*Computational method and validation.*—Our calculations were performed within the generalized gradient approximation (GGA) [10] to the density functional theory (DFT). We employed the SIESTA program package [11], using norm-conserving pseudo potentials [12], and localized basis of numerical pseudo atomic orbitals in the level of doubled orbitals plus polarization orbitals. To verify the quality of the local basis set, some calculations were also performed using a plane wave package, PWSCF [13]. Calculations were carried out in a supercell approach, keeping a vacuum distance of 8 Å between the wall of

the nanotube and its image in the next unit cell. We used 40  $k$  points to sample the one-dimensional Brillouin zone of nitrogen chains with two atoms per unit cell, while for longer unit cells the number of  $k$  points was scaled down keeping the same density of the  $k$  mesh. All systems under study were fully relaxed both with respect to internal atomic positions and to cell size along the nanotube (nitrogen chain) axis including super cell lattice parameters. To test the localized orbital method we performed atomic relaxation of zigzag and armchair periodic nitrogen chains, which have two and four nitrogen atoms per unit cell, respectively. For the zigzag chain we obtained the bond lengths of 1.42 and 1.28 Å, which is in good agreement with results obtained using the plane wave method (1.42, 1.25 Å), as well as with previously reported theoretical values (1.41, 1.32 Å) [14]. For the armchair chain we obtained inter atomic distances of 1.37 and 1.27 Å, which agree well with the results of plane wave calculations (1.35 and 1.25 Å).

We now proceed to the study of the intercalated polymeric nitrogen. We have chosen to use a (5, 5) carbon nanotube as a nanoscale matrix to host polymeric nitrogen chain. Motivating this choice are the following factors: (i) Calculations performed using nanotubes of smaller diameter resulted in nitrogen atoms attaching to the inner nanotube wall due to small carbon-nitrogen distance. (ii) The atomic relaxation of both types of stand-alone nitrogen chains demonstrated that the total energy of the armchair configuration is 27 meV per atom lower than the total energy of the zigzag phase, so the armchair chain was used for all further calculations [15]. (iii) Our unit cell of the intercalated system [Fig. 1(b)], which we shall henceforth refer to as  $N_8@CNT(5, 5)$ , contains 2 elementary unit cells of nitrogen chain (8 atoms) and 3 elementary rings of the CNT. This unit cell was used to calculate band structures and density of states, and to perform *ab initio* molecular dynamics calculations. Imposing these com-

mensurability conditions between the one-dimensional periodicity of the nanotube and that of the nitrogen chain, results in small lattice (7.46 Å) mismatch between the two structures, while keeping the total system size at a computationally effective level. We also took a larger supercell with 9 unit cells for this tube and 24 nitrogen atoms chain on the geometry optimization. The resulted lattice parameters along the  $z$  axis are about 3 times larger than the one for the small unit cell, shown in Fig. 1(a).

*Results and discussions.*—The most striking result of our calculations is the stability of the polymeric nitrogen chain inside the CNT. We should note here that a stand-alone nitrogen chain is an unstable system, with atomic relaxation of a chain consisting of 8 or more atoms in the unit cell resulting in chain dissociation and the formation of  $N_2$  molecules. This is due to the well-known presence of the occupied antibonding state near the top of the valence band of the  $N$ -chain, which causes the formation of localized electronic charge (so-called “lone pairs”) on the neighboring nitrogen atoms. However, upon placement inside the nanotube, the arm-chain polymeric nitrogen is shown to be stable not only under zero-temperature atomic relaxation, but also at ambient conditions through molecular dynamics simulations.

The mechanism of nitrogen chain stabilization by intercalation can be clarified by an electronic structure analysis. Plotted in Fig. 2 is the band structure for the  $N_8@CNT(5, 5)$  system along the one-dimensional Brillouin zone. Band structures for the stand-alone  $N$ -chain and carbon nanotube are also shown for comparison. To highlight the effects of chain-CNT interaction, the stand-alone band structures were calculated using the same atomic coordinates as in the  $N_8@CNT(5, 5)$  system. From a comparison of the bands, we find that the top of the valence bands of  $N_8@CNT(5, 5)$  is a superposition of the valence bands of the stand-alone CNT(5,5) and  $N_8$  systems, which demonstrates that no coupling occurs between the occupied orbitals of the nanotube and  $N$ -chain. However, we see that the first conduction bands are dramatically modified by interaction. It is observed that the first conduction band of the  $N_8$  chain couples with the conduction band of the nanotube, resulting in the formation of lower and upper anticrossing bands, which are indicated in Fig. 2(a) as squares and circles, respectively. This hybridization between the conduction states of the  $N$ -chain and the nanotube is clearly seen from the energy resolved density of electronic states (DOS), projected onto atomic orbitals. We plot in Fig. 2(b) the DOS for the  $N_8@CNT(5, 5)$  system, projected on the orbitals of the nitrogen chain atoms, as well as on the orbitals of the nanotube. Density of states for the stand-alone  $N$ -chain and CNT(5,5) are also shown for comparison. We clearly see a sharp peak, located at about 2.5 eV below the Fermi energy, which corresponds to localized nitrogen lone pair electrons, and which is hardly modified by the presence of

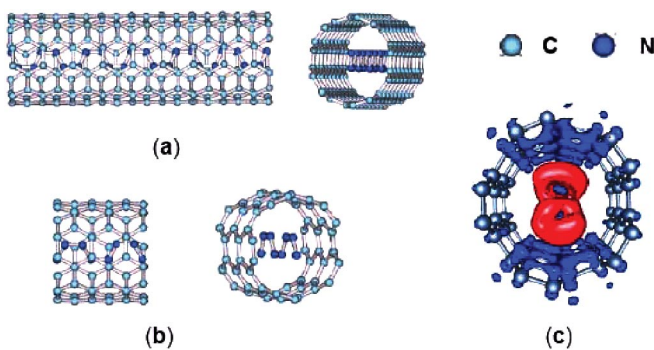


FIG. 1 (color). (a)  $N_{24}@CNT(5, 5)$  with 9 unit cells of (5,5) carbon nanotube. (b)  $N_8@CNT(5, 5)$  with 3 unit cells of (5,5) carbon nanotube. (c) Electronic density of the  $N_8@CNT(5, 5)$  system, minus the sum of electronic densities of stand-alone carbon nanotube and nitrogen chains. Red and blue colors denote the effective positive and negative charge, respectively.

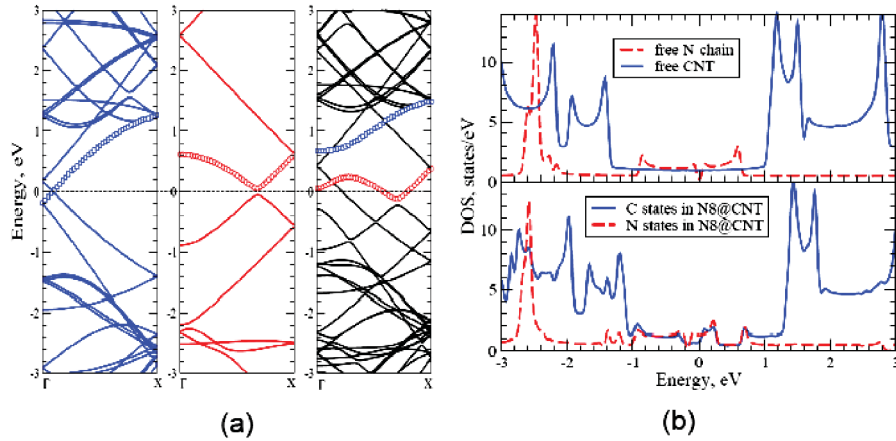


FIG. 2 (color). (a) The band structure of (left) CNT(5,5), (center) N<sub>8</sub> chain, and (right) N<sub>8</sub>@CNT(5, 5). The zero of energy has been set to the Fermi level for CNT(5,5) and N<sub>8</sub>@CNT(5, 5), and to the middle of the energy gap for the N<sub>8</sub> chain. For a stand-alone nanotube, the circles indicate the first conduction band while for the N chain, the squares indicate the first conduction band. For the N<sub>8</sub>@CNT(5, 5) system, the squares and circles indicate the lower and upper anticrossing bands, respectively. (b) Density of electronic states for the N<sub>8</sub>@CNT(5, 5) system (lower panel), as well as for the stand-alone carbon nanotube and nitrogen chain (upper panel). Solid and dashed lines indicate the total DOS, projected on carbon and nitrogen orbitals, respectively. A 0.04 eV broadening has been used.

the nanotube. However, a significant hybridization of electronic states is observed at the Fermi level of the system [0 eV in the Fig. 2(b)], as well as  $\sim 0.8$  eV above  $E_F$ . These two energy regions correspond, respectively, to the position of the lower and upper anticrossing bands, shown in Fig. 2(a).

Figure 2(a) also demonstrates that relatively strong repulsion between the upper and lower anticrossing bands leads to the lower conduction band being pushed down in energy and partially populated. This population of the hybridized conduction band leads to a partial charge transfer from nanotube to nitrogen chain. Indeed, the integrated DOS shows a charge of 0.4 electrons being transferred from nanotube to N chain in the N<sub>8</sub>@CNT(5, 5) system. To get further insight and to illustrate the effect of the charge transfer, we calculated the electronic density redistribution for the N<sub>8</sub>@CNT(5, 5) system. In Fig. 1(c) we plot the difference between the electronic density of the N<sub>8</sub>@CNT(5, 5) system and the sum of electronic densities of stand-alone nitrogen chain and carbon nanotube. The charge transfer, resulting in net effective positive charge on the inner wall of the nanotube and net negative charge on the nitrogen chain, creates an effective electric field inside the nanotube, which, in turn, stabilizes the N chain. We also see that the charge redistribution happens primarily in the plane of the N chain where the C-N distance is minimal, which serves to stabilize the chain from possible rotations.

Finally, to complete our study we performed constant-temperature constant-volume molecular dynamics simulations of the N<sub>8</sub>@CNT(5, 5) system. Calculations were performed for 2 ps time period at  $T = 300$  K conditions. The evolution of bond lengths as temperature is given in

Fig. 3(a) and 3(b). For the two bond lengths in arm-chain polymeric nitrogen, they evolve slightly in an alternative way between 1.2 to 1.38 Å. In the whole simulation, the N<sub>8</sub>@CNT(5, 5) system remains stable. To rigorously verify stability of this system, we also have two additional calculations: (1) a random displacement calculation of nitrogen atoms in which the structure is fully optimized after the

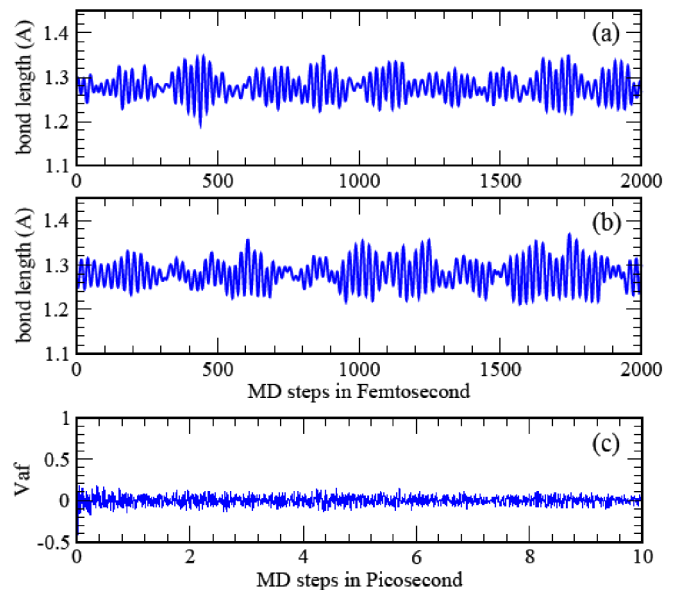


FIG. 3 (color online). (a)–(b) Constant-temperature constant-volume molecular dynamics simulation shows the evolution of bond lengths as temperature. (c) The velocity autocorrelation function (VAF) in time from constant-volume molecular dynamic simulation with  $3 \times 1$  supercell containing 204 atoms shows very strong oscillation behavior, indicating stability.

positions of nitrogen atoms are randomly displaced by 6% of their interatomic distance, bond angles and dihedral angles as well, and (2) constant-volume first-principle molecular dynamic simulation for 10 ps with a  $3 \times 1$  supercell containing 204 atoms in total to explore stability of surfaces and defects. The velocity autocorrelation function is shown in Fig. 3(c), where its oscillation behavior remains around zero for 10 ps, indicating that this system is mechanical stable at ambient condition.

In terms of experimental synthesis of this novel system with conventional chemistry methods, it may be more challenging since one-dimensional polynitrogen chain is not mechanical and thermodynamic stable. In addition, it is clear that this system is not simple chemical C-N compound. However, recently developed chemical vaporization deposition (CVD) methods to synthesize nitrogen doped carbon nanotubes ( $CN_x$ ) may be feasible [16]. We have carried out some studies on this field [17] and nitrogen doped bamboo-like structures of carbon nanotubes were found. To increase nitrogen doping percent may have more opportunities to form polymeric nitrogen or polynitrogen in general. Alternatively, it would be more promising using nitrogen-rich energetic compounds, such as 3,6-diazido-1,2,4,5-tetrazine and 4,4',6,6'-tetraazido-2,2'-azo-1,3,5-triazine compounds, for a non-CVD synthesis of carbon nanotubes [18], since thermal decomposition of these compounds yields nitrogen-rich nanolayered, nanoclustered, and nanodendritic carbon nitrides, depending on the different heating processes [19]. Our simulations have shown that nitrogen-rich compounds can be formed in carbon nanotubes [17]. A laser ablation process used in the growth of carbon nanotubes may be also another alternative for the synthesis of this novel system [20].

**Conclusions.**—In conclusion, we have presented a theoretical study of the electronic and structural properties of nanostructured polymeric nitrogen—a new hybrid system, where the polymeric nitrogen chain is encapsulated inside carbon nanotubes. The calculations, performed using an *ab initio* approach, show that the system is stable, and its stability is explained by a charge transfer, induced by hybridization of the conduction states of the nitrogen chain and the carbon nanotube. Furthermore, employing finite-temperature molecular dynamics simulations, we demonstrated the stability of nanostructured polymeric nitrogen at ambient conditions. This result offers a new and original path towards the synthesis of nitrogen-based high-energy-

density materials as a high-performance green ingredient for future munitions.

---

\*To whom correspondence should be addressed.  
hakima.abou-rachid@drdc-rddc.gc.ca

- [1] M. I. Eremets, A. G. Gavriliuk, I. A. Trojan, D. A. Dzivenko, and R. Boehler, *Nat. Mater.* **3**, 558 (2004).
- [2] K. O. Christe, *Propellants Explosives Pyrotechnics* **32**, 194 (2007).
- [3] C. Mailhot, L. H. Yang, and A. K. McMahan, *Phys. Rev. B* **46**, 14 419 (1992).
- [4] F. Zahariev, S. V. Dudiy, J. Hooper, F. Zhang, and T. K. Woo, *Phys. Rev. Lett.* **97**, 155503 (2006).
- [5] W. D. Mattson, D. Sanchez-Portal, S. Chiesa, and R. M. Martin, *Phys. Rev. Lett.* **93**, 125501 (2004).
- [6] T. Barbee, *Phys. Rev. B* **48**, 9327 (1993).
- [7] S. H. Kim and M. R. Zachariah, *Adv. Mater.* **16**, 1821 (2004).
- [8] Y. Wang, S. Malhotra, and Z. Iqbal, *Mater. Res. Soc. Symp. Proc.* **800**, 351 (2004).
- [9] T. M. Tillotson, A. E. Gash, R. L. Simpson, L. W. Hrubesh, J. H. Satcher, Jr., and J. F. Poco, *J. Non-Cryst. Solids* **285**, 338 (2001).
- [10] J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.* **80**, 891 (1998).
- [11] J. M. Soler, E. Artacho, J. D. Gale, A. García, J. Junquera, P. Ordejón, and D. Sánchez-Portal, *J. Phys. Condens. Matter* **14**, 2745 (2002).
- [12] N. Troullier and J. L. Martins, *Phys. Rev. B* **43**, 1993 (1991).
- [13] S. Baroni, A. Dal Corso, S. de Gironcoli, and P. Giannozzi, <http://www.pwscf.org>.
- [14] A. Pohl, H. Meider, and M. J. Springborg, *Mol. Struct. Theochem.* **305**, 165 (1994).
- [15] Structural relaxation of the zigzag nitrogen chain, intercalated in a (5,5) carbon nanotube, showed its transformation to the stable armchair configuration.
- [16] Chi-Y. Chai, Q. F. Zhang, and J. L. Wu, *Carbon* **44**, 687 (2006).
- [17] H. Abou-Rachid, A. Hu, D. Arato, X. Sun, and S. Desilets (to be published).
- [18] C. Ye, H. Gao, J. A. Boatz, G. W. Drake, B. Twamley, and J. M. Shreeve, *Angew. Chem., Int. Ed.* **45**, 7262 (2006).
- [19] M. H. Huynh, M. A. Hisky, J. G. Archuleta, E. L. Roemer, and R. Gilardi, *Angew. Chem., Int. Ed.* **44**, 737 (2005).
- [20] C. D. Scott, S. Arepalli, P. Nikolaev, and R. E. Smalley, *Appl. Phys. A* **72**, 573 (2001).